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(54) Synergistic herbicide combinations and method of application.

(57) A synergistic herbicidal composition comprising a mixture of: (a) a herbicidally effective amount of 2-(2-chloro-4-methanesulfonylbenzoyl)-1,3-cyclohexanedione; and (b) a herbicidally effective amount of a compound selected from the group consisting of 2-chloro-4-(ethylamino)-6-(isopropyl-amino)-s-triazine, 3-amino-2,5-dichlorobenzoic acid, and 2-chloro-N-isopropylacetanilide, and mixtures thereof; at a weight ratio of (a) to (b) of from about 0.1:1 to about 20:1.

SYNERGISTIC HERBICIDE COMBINATIONS AND METHOD OF APPLICATIONBackground of the Invention

The protection of crops from weeds and other vegetation which inhibit crop growth is a constantly recurring problem in agriculture. To help combat this problem researchers in the field of synthetic chemistry have produced an extensive variety of chemicals and chemical formulations effective in the control of such unwanted growth. Chemical herbicides of many types have been disclosed in the literature and a large number are in commercial use.

In some cases, active herbicides have been shown to be more effective in combination than when applied individually. The result is often termed "synergism," since the combination demonstrates a potency or activity level exceeding that which it would be expected to have, based on a knowledge of the individual potencies of the components. The present invention resides in the discovery that certain cyclohexanediones and other chemical compounds already known individually for their herbicidal potency, display this synergism when applied in combination.

The Prior Art

The compounds which can be combined to form the synergistic herbicidal compositions of this invention are already known in the art as herbicides. One such compound is 2-(2-chloro-4-methanesulfonylbenzoyl)-1,3-cyclohexanedione. This compound is disclosed in European Patent Publication No. 013,796, published 4-4-85. It is also disclosed and claimed in U.S. Application Serial No. 634,408. Another of the compounds used in the synergistic compositions of the invention is 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, commonly known as Atrazine. Still another compound used in the synergistic herbicidal compositions of this invention is 3-amino-2,5-dichlorobenzoic acid, commonly known as Chloramben, described and claimed in U.S. Patents 3,014,063 and 3,174,842. Yet another compound used in the synergistic compositions of this invention is 2-chloro-4-N-isopropylacetanilide, commonly known as Propachlor.

Description of the Invention

It has now been discovered that synergism in the control of undesirable vegetation is exhibited by compositions comprising a mixture of the following components:

(a) a herbicidally effective amount of 2-(2-chloro-4-methanesulfonylbenzoyl)-1,3-cyclohexandione; and

(b) a herbicidally effective amount of a compound selected from the group consisting of 3-(amino-2,5-dichlorobenzoic acid, 2-chloro-N-isopropylacetanilide or 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, and mixtures thereof.

Another embodiment of this invention is a method of controlling undesirable weed pests, and this method comprises applying the synergistic compositions of the invention to the locus where control is desired.

The terms "synergism" and "synergistic" are used herein to convey the result observed when a combination of herbicides demonstrates a potency in excess of that which the combination would be expected to produce on the basis of the potencies of each herbicide applied individually.

The term "herbicide" is used herein to denote a compound which controls or modifies the growth of plants. The term "herbicidally effective amount" is used to indicate the quantity of such a compound or combination of such compounds which is capable of producing a controlling or modifying effect. Controlling or modifying effects include all deviations from natural development, for example: killing, retardation, leaf burn, dwarfing and the like. The term "plants" is used to include all post-emergent vegetation, ranging from seedlings to established vegetation.

As previously mentioned, the synergistic compositions of this invention all employ chemical compounds previously known for their herbicidal activity. One of these compounds, 2-(2-chloro-4-methanesulfonylbenzoyl)-1,3-cyclohexanedione, is disclosed in European Patent Publication No. 013,786, published 4-4-85, and it is also disclosed and claimed in U.S. Application Serial No. 634,408. Still another compound, 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, commonly known as Atrazine, is commercially sold under various tradenames, and is described in the

Herbicide Handbook of the Weed Science Society of America, 5th Edition, 1983. Another of the compounds used in the synergistic combinations of the invention, 3-amino-2,5-dichlorobenzoic acid, is commercially available under a number of tradenames and is described on page 92 of the Herbicide Handbook of the Weed Science Society of America, 5th Edition, 1983. Yet another compound used in the synergistic compositions of this invention is 2-chloro-4-N-isopropylacetanilide, is described on pages 401 and 402 of the Herbicide Handbook of the Weed Science Society of America, 5th Edition, 1983.

10 These compounds are effectively used in the synergistic compositions of the invention at ratios of Compound (a) to Compound (b) as set forth above, ranging from about 0.01:1 to about 20:1. Preferably, the ratio of Compound (a) to Compound (b) is from about 0.1:1 to about 10:1.

Herbicidal Test Data

15 Synergism for the compositions of this invention was measured in accordance with the following test:

Aluminum pans measuring 9 x 6 x 4 inches (cm) were filled with a sandy loam soil and 6 furrows were impressed across the width of each flat. A number of weed species were seeded into furrows and covered with soil. Along with the seed species were two corn hybrids which were 20 inserted to determine the extend of damage, if any, upon plant species.

The weed species were as follows:

<u>Abbreviation</u>	<u>Common Name</u>	<u>Scientific Name</u>
YNS	yellow nutsedge	<u>Cyperus esculentus</u>
PNS	purple nutsedge	<u>Cyperus rotundus</u>
RJG	rhizome johnsongrass	<u>Sorghum halepense</u>
FP	fall panicum	<u>Panicum dichotomiflorum</u>
WPM	wild proso millet	<u>Panicum milaceum</u>
GG	goosegrass	<u>Eleusine indica</u>
SC	shattercane	<u>Sorghum bicolor</u>
YFT	yellow foxtail	<u>Setaria lutescens</u>
GFT	green foxtail	<u>Setaria viridis</u>
PW	redroot pigweed	<u>Amaranthus retroflexus</u>

AMG	annual morningglory	<u>Ipomoea purpurea</u>
SP	sicklepod	<u>Cassia obtusifolia</u>
VL	velvetleaf	<u>Abutilon theophrasti</u>
LCG	large crabgrass	<u>Digitaria ischaemum</u>
JG	johnsongrass	<u>Sorghum halepense</u>

The plant species were as follows:

CN	corn	<u>Zea maize</u> (L.)
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Chemical solutions, which in the case of pre-emergence testing were sprayed the same day of seeding, were prepared as follows:

All compounds were of technical grade, except Prowl which was what is termed a 4E formulation, which means a 4 pound per gallon emulsion concentrate. All of the technical grade compounds were either applied singly, or applied in conjunction with the synergistic herbicidal compound, by diluting the technical grade compounds with acetone and water at 1:1 ratio water and applying at a spray volume of 25 gal/acre. The quantity of active ingredient for each compounds which was applied is indicated under the heading "Application Rate".

In the case of post-emergent testing, the weed and plant species were allowed to sprout and application was made approximately 2 weeks after planting.

The various rates of application are indicated in the tables under "Application Rate".

Flats were then placed in a greenhouse, and watered by overhead sprinkling. Air temperatures ranged from 18°C to 27°C. Flats were kept moist during the course of each experiment.

After treatment, each row of seedlings was visually rated for growth control due to all factors of injury. In pre-emergence testing the ratings were done 28 days after treatment. In post-emergent testing, the rating was done 21 days after treatment. Untreated flats of seedlings were used for comparison, zero percent injury or growth control is equivalent to growth in control flats. One hundred percent growth control is equivalent to complete kill.

Herbicide interaction responses were evaluated by use of Limpel's formula (Limpel, L.E., et al., 1962, "Weed Control by Dimethyl-tetrachloroterephthalate Alone and in Certain Combinations," Proc. NEWCC, 16: 48-53):

$$E = X + Y - \frac{XY}{100}$$

where E = expected response

where X = observed (O) value or percent growth control when the herbicide is applied singly; and

Y = observed (O) value or percent growth control when the second herbicide is applied singly.

5 A response is synergistic when an observed value is greater than the calculated value, a synergistic response is understood to be one in which the interaction response is greater than the sum of responses from the individual chemical treatments. An antagonistic response is the opposite situation.

10 In the tables which follows:

E = expected activity

O = observed activity

R = result, i.e., additive (AD), antagonistic (A) or synergistic (S)

TABLE 1
Pre-Emergence

Application Treatment	Rate lb/A	YNS			PNS			RJG			CN			CN		
		O	E	R	O	E	R	O	E	R	O	E	R	O	E	R
X-100	1/4	85			65			0			0			0		
	1/2	90			95			30			0			0		
ATRAZINE	1/4	0			0			0			0			0		
	1/2	0			0			0			0			0		
LASSO	1/2	100			80			0			0			0		
	1	100			100			0			0			0		
AMIBEN	1	0			0			30			0			15		
	2	0			65			50			70			25		
PROWL	1/4	0			0			20			0			0		
	1/2	0			0			0			50			10		
RAMROD	2	20			30			0			0			0		
	3	100			90			0			0			0		
X-100	1/4+1/4	90	85	S	80	65	S	20	0	S	0	0	0	0	0	0
+ ATRA-	1/2+1/4	95	90	S	90	95	A	30	30	AD	0	0	0	0	0	0
ZINE	1/2+1/2	98	95	S	95	65	S	20	0	S	0	0	0	0	0	0
LASSO	1/2+1/2	95	90	S	95	95	AD	30	30	AD	0	0	0	0	0	0
X-100	1/4+1/2	100	100	AD	95	93	S	15	0	S	0	0	0	0	0	0
+ LASSO	1/2+1/2	98	100	A	85	99	A	40	30	S	0	0	0	0	0	0
X-100	1/4+1	95	100	A	95	100	A	20	0	S	0	0	0	10	0	0
+ AMIBEN	1/2+1	95	100	A	100	100	AD	60	30	S	10	0	0	0	0	0
X-100	1/4+1	95	85	S	95	65	S	20	30	A	0	0	30	15		
+ AMIBEN	1/2+1	98	90	S	98	95	S	50	51	A	40	0	30	15		
X-100	1/4+2	95	85	S	95	88	S	30	50	A	25	70	40	25		
+ PROWL	1/2+2	95	90	S	98	98	AD	75	65	S	65	70	50	25		
X-100	1/4+1/4	95	85	S	95	65	S	10	20	A	20	0	0	0	0	0
+ PROWL	1/2+1/4	95	90	S	98	95	S	55	44	S	25	0	30	0	0	0
X-100	1/4+1/2	95	90	S	95	95	AD	10	0	S	40	50	20	10		
+ RAMROD	1/2+1/2	95	90	S	95	95	AD	10	30	A	45	50	40	10		
X-100	1/4+2	95	88	S	98	76	S	5	0	S	0	0	0	0	0	0
+ RAMROD	1/2+2	95	92	S	99	97	S	15	30	A	0	0	0	0	0	0
X-100	1/4+3	100	100	AD	100	97	S	5	0	S	0	0	0	0	0	0
+ RAMROD	1/4+3	95	100	A	95	100	A	65	30	S	0	0	0	0	0	0
CONTROL	-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

X-100 = 2-(2-chloro-4-methanesulfonylbenzoyl)-1,3-cyclohexanedione
 Atrazine = 2-chloro-4-(ethylamino)-6-isopropylamino)-s-triazine
 Lasso = 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide
 Amiben = 3-amino-2,5-dichlorobenzoic acid
 Prowl = N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine
 Ramrod = 2-chloro-N-isopropylacetanilide

TABLE 2
Pre-Emergence

Application Rate lb/A	FP			WFM			CG			SC			YFT			GFT			
	O	E	R	O	E	R	O	E	R	O	E	R	O	E	R	O	E	R	
X-100	1/4	20	95	100	100	15	95	95	90	95	95	10							
	1/2	100	100									65							
ATRAZINE	1/4	60	0	65	0	0	45			30									
	1/2	70	40	95	0	0	80			60									
LASSO	1/2	100	95	100	90	90	90	90	90	100	100								
	1	100	98	100	100	100													
AMIBEN	1	100	95	95	100	0	75			45									
	2	95	95	100	100	0	85			85									
PROWL.	1/4	100	95	100	90	90	95			95									
	1/2	100	100	100	100	100	100	100	100	100	100	100							
RAMROD	2	75	50	95	0	0	90			95									
	3	100	90	100	100	0	90			100									
X-100	1/4+1/4	100	68	S	100	95	S	100	100	AD	100	15	S	90	97	A	100	37	S
+	1/2+1/4	100	100	AD	100	100	AD	100	100	AD	95	95	AD	95	94	S	100	75	S
ATRA-	1/2+1/2	95	75	S	100	97	S	100	100	AD	90	15	S	90	99	A	100	64	S
ZINE	1/2+1/2	100	100	AD	100	100	AD	100	100	AD	100	95	S	100	98	S	100	86	S
X-100	1/4+1/2	100	100	AD	100	100	AD	100	100	AD	90	91	A	85	99	A	100	100	AD
+	1/2+1/2	100	100	AD	100	100	AD	100	100	AD	98	93	A	100	99	S	100	100	AD
LASSO	1/4+1	100	100	AD	100	100	AD	100	100	AD	95	100	A	100	99	A	100	100	AD
	1/2+1	100	100	AD	100	100	AD	100	100	AD	98	100	A	100	99	S	100	100	AD
X-100	1/4+1	100	100	AD	100	100	AD	100	100	AD	100	15	S	98	99	A	100	50	S
+	1/2+1	100	100	AD	100	100	AD	100	100	AD	98	95	S	98	98	AD	100	81	S
AMIBEN	1/4+2	100	96	S	100	100	AD	100	100	AD	70	15	S	80	99	A	100	86	S
	1/2+2	100	100	AD	100	100	AD	100	100	AD	98	95	S	95	98	A	95	95	AD

TABLE 2
(continued)

<u>Application Rate</u>	<u>FP</u>	<u>WPM</u>	<u>GC</u>	<u>SC</u>	<u>YFT</u>	<u>GFT</u>
<u>Treatment</u>	<u>O E R</u>					
X-100 1/4+1/4	100 100 AD	98 100 A	100 100 AD	95 91 S	100 100 AD	100 95 S
+ 1/2+1/4	100 100 AD	100 100 AD	100 100 AD	98 99 A	100 99 S	100 98 S
PROWL 1/4+1/2	100 100 AD	100 100 AD	100 100 AD	98 100 A	100 100 AD	100 100 AD
1/2+1/2	100 100 AD					
X-100 1/4+2	100 80 S	100 97 A	100 100 AD	90 15 S	100 99 S	100 95 S
+ 1/2+2	100 100 AD	100 100 AD	100 100 AD	100 95 S	100 99 S	100 98 S
RAMROD 1/4+3	100 100 AD	100 100 AD	100 100 AD	65 15 S	100 100 AD	100 100 AD
1/4+3	100 100 AD	100 100 AD	100 100 AD	85 95 A	100 100 AD	100 100 AD
CONTROL -	0 0 0	0 0 0	0 0 0	0 0 0	0 0 0	0 0 0

TABLE 3
Pre-Emergence

Application	Rate	FW	AMG	SP	VL	LCG	JG
Treatment	lb/A	O E R	O E R	O E R	O E R	O E R	O E R
X-100	1/4	100	100	20	100	75	20
	1/2	70	100	70	100	100	95
ATRAZINE	1/4	100	100	0	100	10	0
	1/2	100	100	55	100	10	45
LASSO	1/2	90	0	60	65	90	100
	1	95	10	85	60	100	100
AMIBEN	1	40	0	50	100	90	95
	2	80	0	65	100	90	98
PROWL	1/4	70	0	0	0	80	80
	1/2	85	0	0	85	100	95
RAMROD	2	60	0	0	0	50	75
	3	100	10	60	30	85	95
X-100	1/4+1/4	100	100	AD	60	20	S
+	1/2+1/4	100	100	AD	100	100	AD
ATRA-	1/2+1/2	100	100	AD	90	70	95
ZINE	1/2+1/2	100	100	AD	98	64	95
LASSO	1/4+1/2	100	100	AD	95	86	56
	1/2+1	100	97	S	100	100	S
	1/4+1	100	100	AD	100	88	56
	1/2+1	100	98	S	98	88	95
X-100	1/4+1/2	100	100	AD	98	95	S
+	1/2+1/2	100	97	S	100	100	AD
AMIBEN	1/4+2	100	100	AD	90	100	AD
	1/2+2	100	94	S	100	100	AD
X-100	1/4+1	98	100	A	100	100	S
+	1/2+1	100	82	S	100	100	AD
AMIBEN	1/4+2	100	100	AD	98	95	99
	1/2+2	100	94	S	80	72	S
					85	89	100
					A	100	99

TABLE 3
(continued)

TABLE 4
Post-Emergence

TABLE 5
Post-Emergence

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Post-Emigration
TABLE 6

Application rates for the compositions of this invention will depend upon the weeds to be controlled and the degree of control desired. In general, the compositions of this invention are most efficiently employed at a rate of 0.01 to 50 pounds per acre (0.011 to 56 kilograms per hectare) of the active ingredients, preferably 0.1 to 25 pounds per acre (0.11 to 28 kilograms per hectare).

The compositions of the present invention show synergistic activity as herbicides in controlling the growth of undesirable vegetation when applied to such vegetation in pre- or postemergence application. The compositions are generally embodied in formulations which contain inert or occasionally active ingredients or diluent carriers in addition to the active compounds. Examples of such ingredients or carriers are water, organic solvents, surface active agents, oil, water-in-oil emulsions, wetting agents, dispersing agents, and emulsifying agents. The herbicidal formulations generally take the form of wettable powders, solutions or emulsifiable concentrates.

Wettable powders are finely divided compositions comprising a particulate carrier impregnated with the herbicidal compound and additionally containing one or more surface active agents. The surface active agent promotes rapid dispersion of the powder in aqueous medium to form stable, sprayable suspensions. A wide variety of surface active agents can be used, for example, long chain fatty alcohols and alkali metal salts of the sulfated fatty alcohols; salts of sulfonic acid; esters of long chain fatty acids; and polyhydric alcohols, in which the alcohol groups are free, omega-substituted polyethylene glycols of relatively long chain length.

The herbicidal compositions can also be applied to the foliage in the form of a solution in a suitable solvent. Solvents frequently used in herbicidal formulations include kerosene, fuel oil, xylene, petroleum fractions with boiling ranges above xylene, and aromatic petroleum fractions rich in methylated naphthalenes.

The most preferred formulations are emulsifiable concentrates which consist of an oil solution of the herbicide along with an emulsifying agent. Prior to use the concentrate is diluted with water to form a suspended emulsion of oil droplets. The emulsifiers used are usually a mixture of anionic and nonionic surfactants. Other additives such as spreading agents and stickers can be included in the emulsifiable concentrate.

The formulations described above can be applied to the vegetation sought to be controlled in any conventional manner either before or after the vegetation has emerged from the soil. The vegetation can be in any stage of development after emergence, ranging from seedlings to fully grown plants. Application can be achieved by any conventional technique such as the use of ground spraying equipment or aircraft-mounted sprayers. Various other application techniques will be apparent to one skilled in the pesticide art.

WHAT IS CLAIMED IS:

1. A synergistic herbicidal composition comprising a mixture of:
 - (a) a herbicidally effective amount of 2-(2-chloro-4-methane-sulfonylbenzoyl)-1,3-cyclohexanedione; and
 - 5 (b) a herbicidally effective amount of a compound selected from the group consisting of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, 3-amino-2,5-dichlorobenzoic acid, and 2-chloro-N-isopropylacetanilide, and mixtures thereof;
at a weight ratio of (a) to (b) of from about 0.1:1 to about 20:1.
- 10 2. The composition of Claim 1 wherein (b) is 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine.
3. The composition of Claim 1 wherein (b) is 3-amino-2,5-dichlorobenzoic acid.
- 15 4. The composition of Claim 1 wherein (b) is 2-chloro-N-isopropylacetanilide.
5. A synergistic herbicidal composition comprising a mixture of:
 - (a) a herbicidally effective amount of 2-(2-chloro-4-methane-sulfonylbenzoyl)-1,3-cyclohexanedione;
 - 20 (b) a herbicidally effective amount of a compound selected from the group consisting of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, 3-amino-2,5-dichlorobenzoic acid, and 2-chloro-N-isopropylacetanilide, and mixtures thereof; and
(c) an inert diluent carrier,
25 at a weight ratio of (a) to (b) of from about 0.01:1 to about 20:1.
6. The composition of Claim 5 wherein (b) is 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine.
- 30 7. A method of controlling undesirable vegetation which comprises the application to said vegetation of a herbicidal composition comprising

(a) a herbicidally effective amount of 2-(2-chloro-4-methanesulfonylbenzoyl)-1,3-cyclohexanedione;

(b) a herbicidally effective amount of a compound selected from the group consisting of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, 3-amino-2,5-dichlorobenzoic acid, and 2-chloro-N-isopropylacetanilide, and mixtures thereof,
5 at a weight ratio of (a) to (b) of from about 0.1:1 to about 20:1.

8. The method of Claim 7 wherein (b) is 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine.

10 9. The method of Claim 7 wherein (b) is 3-amino-2,5-dichlorobenzoic acid.

10. The method of Claim 7 wherein (b) is 2-chloro-N-isopropylacetanilide.

11. A synergistic herbicidal composition comprising a mixture of:

(a) a herbicidally effective amount of 2-(2-chloro-4-methane-sulfonylbenzoyl)-1,3-cyclohexanedione; and

(b) a herbicidally effective amount of a compound selected from the group consisting of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, 3-amino-2,5-dichlorobenzoic acid, and 2-chloro-N-isopropylacetanilide, and mixtures thereof;

at a weight ratio of (a) to (b) of from about 0.1:1 to about 20:1.

10 12. The composition of Claim11 wherein (b) is 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine.

13. The composition of Claim11 wherein (b) is 3-amino-2,5-dichlorobenzoic acid.

14. The composition of Claim11 wherein (b) is 2-chloro-N-isopropylacetanilide.

15. A synergistic herbicidal composition comprising a mixture of:

(a) a herbicidally effective amount of 2-(2-chloro-4-methane-sulfonylbenzoyl)-1,3-cyclohexanedione;

(b) a herbicidally effective amount of a compound selected from the group consisting of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, 3-amino-2,5-dichlorobenzoic acid, and 2-chloro-N-isopropylacetanilide, and mixtures thereof; and

(c) an inert diluent carrier,

25 at a weight ratio of (a) to (b) of from about 0.01:1 to about 20:1.

16. The composition of Claim15 wherein (b) is 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine.